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# 学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 邢 飛龍

## 学 位 論 文 題 名

### Developing a Highly Efficient Multimetallic Catalyst for CO<sub>2</sub>-assisted oxidative dehydrogenation and dry reforming of propane

(CO<sub>2</sub> によるプロパンの酸化脱水素および改質反応に有効な多元素合金触媒の開発)

Attempts have long been made to improve the performance of metal catalysts by alloying, but it is difficult to achieve performance improvements by simply combining two metals. Therefore, fundamental innovation in catalyst design guidelines is necessary to develop high-performance catalysts that can meet the growing needs of society. In this regard, two approaches have been used: (i) pseudo-binary alloy, which is ternary alloys represented as  $A_m(B_{1-x}C_x)_n$ , where one metal site of the intermetallic  $A_mB_n$  is partially replaced by third metal C, and (ii) High-entropy intermetallics (HEIs), which are multi-metallic alloys with five or more elements whose specific crystal structure is derived from the parent binary intermetallics.

**Chapter 2** showed that Pt–Co–In ternary alloy on CeO<sub>2</sub> exhibited a highly efficient catalyst for CO<sub>2</sub>-ODP. Both the C<sub>3</sub>H<sub>8</sub> dehydrogenation and CO<sub>2</sub> reduction smoothly proceed on the Pt–Co active site to form 2H and O, as well as the main products: C<sub>3</sub>H<sub>6</sub> and CO. Alloying with In enhances the C<sub>3</sub>H<sub>6</sub> selectivity due to the ensemble effect and decreases the amount of coke that accumulates on the catalyst surface. The doped Co improves the adsorption strengths of the C and H species, which promotes the activation of C<sub>3</sub>H<sub>8</sub> and CO<sub>2</sub>. The O atoms oxidize the eliminated H to form H<sub>2</sub>O or combust coke on the alloy surface or neighboring CeO<sub>2</sub> sites. Moreover, CeO<sub>2</sub> can facilitate coke combustion via a Mars-van Krevelen-type mechanism, which significantly enhances the coke resistance and catalyst stability. Pt–Co–In/CeO<sub>2</sub> exhibits outstanding catalytic activity, C<sub>3</sub>H<sub>6</sub> selectivity, long-term stability, and CO<sub>2</sub> utilization efficiency, all of which are greater than typical values ever reported. In **Chapter 3**, I further designed and prepared a PtSn-based HEIs catalyst for higher coke resistant and thermal stability than those of Pt–Co–In/CeO<sub>2</sub>. I focused on intermetallic PtSn and its Pt and Sn sites were partially substituted with Ni/Co and In/Ga, resulting in nanoparticles with a HEI structure of (PtCoNi)(SnInGa). The multi-metallization sufficiently isolates Pt atoms, preventing propylene decomposition and coke formation. The incorporation of Ni and Co significantly enhanced the ability to activate CO<sub>2</sub>. Doping In(Ga) into the Sn site improved catalyst stability, probably due to the enhanced entropy effect. The combination of these abilities significantly enhances coke resistance and catalyst lifetime. Furthermore, because of the increased thermal stability, multi-metallization also prevents nanoparticle sintering. The HEI/CeO<sub>2</sub> catalyst shows much greater catalyst life and specific activity than Pt–Co–In/CeO<sub>2</sub>. In **Chapter 4**, I further applied the Pt–Co–In ternary alloy system to dry reforming of propane (DRP), which has attracted much attention as a syngas production technology for liquid fuels with a low H<sub>2</sub>/CO ratio. The PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> for the DRP reaction with high selectivity and stability even over 100 h. The results show that the catalytic behavior of these catalysts is highly sensitive to the amount of cobalt doping. By controlling the amount of cobalt doping, the catalytic activity of PtCo<sub>2</sub>In<sub>3</sub>/CeO<sub>2</sub> catalysts can be improved, and the C–H/C–C bond of propane can be selectively cleaved in the presence of CO<sub>2</sub>.

In summary, the study in this thesis not only provides excellent catalytic performances in conversion of light alkane and CO<sub>2</sub>, but also opens a new window for the design of multi-metallic catalysts for challenging molecular conversions.